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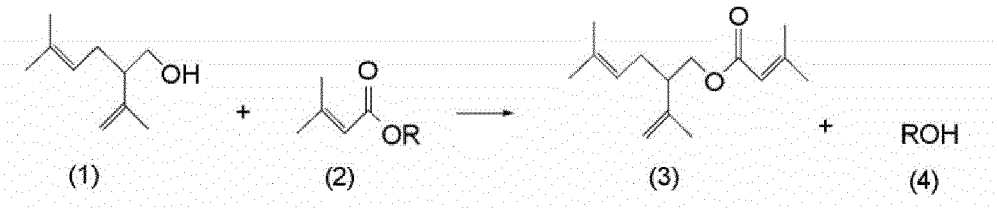
(54) METHOD FOR PRODUCING 2-ISOPROPENYL-5-METHYL-4-HEXEN-1-YL 3-METHYL-2-BUTENOATE

(57) Provided is a method for industrially producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, which is, for example, a sex pheromone substance of vine mealybug. More specifically, there is provided a method for producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, comprising a step of transesterifying 2-isopropenyl-5-methyl-4-hexen-1-ol represented by Formula (1) with alkyl senecioate represented by General Formula (2) in the presence of a catalyst, while distilling off an alcohol represented by General Formula (4) formed as a by-product, to obtain 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate represented by Formula (3).



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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (generic name: lavandulyl senecioate) as a sex pheromone component of vine mealybug (scientific name: Planococcus ficus).

2. Description of the Related Art

[0002] Vine mealybug (scientific name: Planococcus ficus) is known as one of major insects of grapevines and damages fruits of grapevines, causing serious problems such as reductions in the yield and the crop quality. At the present time, insecticides are used to control the vine mealybug without sufficient success. Because of concerns about the environment and human health affected by the use of insecticides, there is a demand for the development of novel insect pest control methods such as mating disruption and mass trapping by using sex pheromone substances.

[0003] The sex pheromone substance that is secreted by females of the vine mealybug and is used for reproductive behavior is 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (generic name: lavandulyl senecioate), which has been reported by Diane M. Hinkens et al. (Tetrahedron Letters 42 (2001) 1619-1621).

[0004] The existing method for producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate is exemplified by the method reported by Diane M. Hinkens et al. (Tetrahedron Letters 42 (2001) 1619-1621). In the method, senecioyl halide prepared by halogenation of senecioic acid is reacted with 2-isopropenyl-5-methyl-4-hexen-1-ol in the presence of an organic base. However, when the compound is produced in an industrial scale by the method of Hinkens et al., by-products are formed during the purification by distillation to lower the yield. To address the problem, WO 2008/075468 discloses the method in which an unpurified 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate is heat-treated in the presence of a basic substance and then is purified by distillation.

[0005] Another production method is also reported in WO 2006/109570. In the method, a sulfonate ester prepared from 2-isopropenyl-5-methyl-4-hexen-1-ol and an organic sulfonyl halide is reacted with senecioic acid in the presence of a basic substance.

SUMMARY OF THE INVENTION

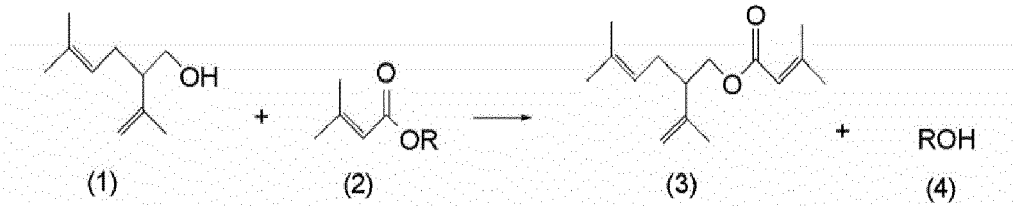
[0006] The production method described in WO 2008/075468 unfortunately requires a plurality of production steps. In addition, after the reaction, the unpurified 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate is required to be heat-treated for a long period of time in the presence of a basic substance such as sodium carbonate, thereby the method requiring a lot of time. The production method described in WO 2006/109570 requires a plurality of production steps, and the reaction is complicated. In addition, a large amount of a solid basic substance such as potassium carbonate or sodium carbonate is used in the reaction of a sulfonate ester compound and senecioic acid, and thus a large amount of a solvent is required in order to maintain stirring of the reaction solution, resulting in a small amount of product per volume of the reactor. It is known that when a sex pheromone substance is mixed with an isomer thereof such as a geometric isomer, a positional isomer and an optical isomer, the activity thereof can be suppressed. In the production method described in WO 2006/109570, the reaction is carried out with heat for a long period of time in the presence of a basic substance, and thus 1.5 to 2.0% of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which is a positional isomer of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, is unfortunately produced as a by-product. As described above, in the existing production methods, large amounts of isomers are formed as by-products, and the productivity is low. Such methods have problems for the industrial mass production.

[0007] In view of the above circumstances, the present invention has been made to solve the problems in the conventional methods. An object of the present invention is to provide a method for industrially producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, which is, for example, a sex pheromone substance of vine mealybug.

[0008] The inventors of the present invention have intensively studied in order to solve the problems, and consequently have found that transesterification of alkyl senecioate (2) in place of senecioyl halide, which is a cause of generating a by-product during distillation, with 2-isopropenyl-5-methyl-4-hexen-1-ol (1) can simply produce 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate at a high yield while production of isomer as a by-product is suppressed and a by-product is not formed during distillation. The reaction can be carried out without a solvent, so that it has been found that the amount of product per volume of the reactor is improved. As a result, the present invention has been completed.

[0009] In one aspect of the present invention, there is provided a method for producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, comprising a step of transesterifying 2-isopropenyl-5-methyl-4-hexen-1-ol represented by Formula (1) with alkyl senecioate represented by General Formula (2) in the presence of a catalyst, while distilling

off an alcohol represented by General Formula (4) formed as a by-product, to obtain 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate represented by Formula (3).



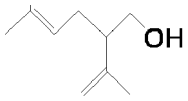
In the above, R is a saturated or unsaturated linear alkyl group having 1 to 6 carbon atoms.

[0010] According to the present invention, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, which is, for example, a sex pheromone substance of vine mealybug, can be efficiently and industrially produced at low cost.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention will now be described in detail.

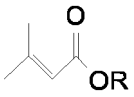
[0012] 2-Isopropenyl-5-methyl-4-hexen-1-ol (1) shown below can be produced by a known method.



(1)

[0013] Examples of the method for producing 2-isopropenyl-5-methyl-4-hexen-1-ol (1) include the method comprising the steps of subjecting isopentenyl bromide and senecioic acid ester to a condensation reaction in sodium amide to obtain an ester, and reducing the ester (Japanese Patent Application Examined Publication No. 39-7756); the method comprising the steps of reacting 2-methyl-2-propenyl tolyl sulfone with isopentenyl bromide to obtain an allyl sulfone compound, reacting the allyl sulfone compound with tributyltin hydride in the presence of azobisisobutyronitrile (AIBN) to obtain a tin compound, and hydroxymethylating the tin compound (Y. Ueno et al., J. Chem. Soc., Chem. Commun., 1980, 683); the method comprising the steps of rearranging 2-methyl-buten-2-yl dimethylacrylate with sodium hydride, and reducing the resulting product with lithium aluminum hydride (US Patent No. 3,781,333); the method comprising the steps of silylating an enone compound, and then subjecting to the Wittig reaction to convert the silyl group into alcohol (I. Fleming et al., Tetrahedron Lett., 37, 38, 6929, 1996); the method comprising the step of rearranging diprenyl ether or 1,1-dimethyl-2-propenyl prenyl ether in the presence of an aluminum compound (Japanese Patent Application Unexamined Publication No. 58-148832); and the method comprising the steps of reacting 3-methyl-2-butenal dimethyl acetal with 3-methyl-1-buten-3-ol in the presence of an acid catalyst to obtain lavandulal, and reducing the lavandulal (Japanese Patent Application Unexamined Publication No. 2002-308815).

[0014] The alkyl senecioate (2) shown below is used for transesterification.



(2)

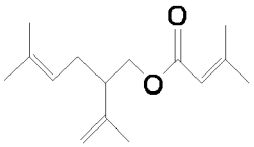
[0015] In the above formula, R represents a saturated or unsaturated linear alkyl group having 1 to 6 carbon atoms.

[0016] Specific examples of the alkyl senecioate include saturated alkyl esters of senecioic acid such as methyl senecioate, ethyl senecioate, n-propyl senecioate and n-butyl senecioate; and unsaturated alkyl esters of senecioic acid such as vinyl senecioate and isopropenyl senecioate. Among them, methyl senecioate, ethyl senecioate, vinyl senecioate and isopropenyl senecioate are preferred, and methyl senecioate and ethyl senecioate are particularly preferred from the viewpoint of easy availability and reactivity.

[0017] The amount of the alkyl senecioate to be used for the transesterification is preferably 1.0 mol to 3.0 mol relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1), and is particularly preferably 1.2 to 2.0 mol relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1) from the viewpoint of reaction rate and cost efficiency.

[0018] By the transesterification, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (3) shown below is pro-

duced as the target compound, together with the alcohol (4) shown below as a by-product.



(3)

ROH (4)

[0019] The alcohol formed as a by-product varies depending on the type of the alkyl senecioate used. Examples of the alcohol include saturated alcohols such as methanol, ethanol, n-propanol and n-butanol; and unsaturated alcohols such as vinyl alcohol and isopropenol. Vinyl alcohol and isopropenol are unstable and immediately converted into acetaldehyde and acetone, respectively. Among them, methanol, ethanol, vinyl alcohol (acetaldehyde after conversion) and isopropenol (acetone after conversion) are preferred, and methanol and ethanol are particularly preferred from the viewpoint of reactivity and separation by distillation.

[0020] Examples of the catalyst to be used for the transesterification include an acid such as hydrochloric acid, sulfuric acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid and Amberlyst 15; an alkali metal salt of alcohol such as sodium methoxide, sodium ethoxide and potassium t-butoxide; a metal carboxylate such as sodium acetate, potassium acetate, calcium acetate, tin acetate, zinc acetate and aluminum acetate; a Lewis acid containing an aluminum atom, such as aluminum trichloride, chloroaluminum ethoxide, dichloroaluminum ethoxide, aluminum methoxide, aluminum ethoxide and aluminum isopropoxide; a Lewis acid containing a zinc atom, such as zinc chloride and zinc bromide; a Lewis acid containing a boron atom, such as boron trifluoride, boron trichloride and boron tribromide; a Lewis acid containing a tin atom, such as tin tetrachloride, dibutyltin dichloride, dibutyltin dimethoxide, dibutyltin oxide, monobutyltin oxide and dibutyltin dichloride; and a Lewis acid containing a titanium atom, such as titanium tetrachloride, titanium tetrabromide, titanium(IV) methoxide, titanium(IV) ethoxide, titanium(IV) isopropoxide and titanium(IV) oxide. Among them, a Lewis acid containing a titanium atom, a Lewis acid containing a tin atom and a Lewis acid containing an aluminum atom are preferred from the viewpoint of reactivity and a small amount of impurity; and titanium(IV) methoxide, titanium(IV) ethoxide, titanium(IV) isopropoxide, dibutyltin dimethoxide, dibutyltin oxide, dibutyltin dichloride, aluminum methoxide, aluminum ethoxide and aluminum isopropoxide are particularly preferred from the viewpoint of yield and a small amount of impurity.

[0021] The amount of the catalyst to be used for the transesterification is preferably 0.001 to 0.5 mol relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1), and is particularly preferably 0.005 to 0.05 mol relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1) from the viewpoint of cost efficiency and yield.

[0022] The transesterification can be carried out commonly without a solvent. However, a solvent can be supplementally used to facilitate the removal of the alcohol formed as a by-product. The solvent can be any solvent that does not adversely affect the reaction, and preferred examples of the solvent include a hydrocarbon solvent such as hexane, benzene, toluene and xylene; and an ether solvent such as tetrahydrofuran, di-n-butyl ether, ethylene glycol dimethyl ether and ethylene glycol diethyl ether.

[0023] The amount of the solvent is not particularly limited. The amount of the solvent is preferably 50 ml to 200 ml relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1), and is particularly preferably 50 ml to 100 ml relative to 1.0 mol of 2-isopropenyl-5-methyl-4-hexen-1-ol (1) from the viewpoint of cost efficiency and reactivity.

[0024] The transesterification is typically carried out under heating and is preferably carried out at a temperature equal to or higher than the boiling point of the alcohol formed as a by-product. For example, when methyl senecioate is used as the alkyl senecioate, the transesterification is carried out preferably at 65°C to 140°C under atmospheric pressure, and is carried out particularly preferably at 80°C to 120°C under atmospheric pressure from the viewpoint of reactivity and a small amount of impurity. When ethyl senecioate is used as the alkyl senecioate, the transesterification is carried out preferably at 80°C to 160°C under atmospheric pressure, and is carried out particularly preferably at 100°C to 140°C under atmospheric pressure from the viewpoint of reactivity and a small amount of impurity.

[0025] During the transesterification, the alcohol formed as a by-product as the reaction progresses is removed by distillation. In order to facilitate the removal of the alcohol formed as a by-product, the reaction can be carried out under reduced pressure.

[0026] The reaction mixture obtained by the transesterification can be purified by distillation in the same reactor or the same distillation apparatus as that used for the transesterification, preferably being subjected neither to reaction termination treatment nor to post-treatment for removing a substance that adversely affects the target compound, so as to obtain 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate as the target compound at high purity and high yield.

[0027] Typically, the purification by distillation is carried out under reduced pressure, and the target compound is distilled preferably at a boiling point of 60 to 150°C/0.013 KPa to 1.333 KPa.

[0028] In the method in accordance with the invention, decrease of the yield due to a by-product formed during the distillation is not observed unlike WO 2008/075468, and 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate as the target compound can be produced at a good yield. The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which is an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, varies depending on distillation conditions when the target compound is isolated by the distillation, but can be suppressed to preferably 0.5% by weight or less, more preferably 0.3% by weight or less, even more preferably 0.15% by weight or less in the isolated fraction. The lower limit of the content of the isomer is preferably 0% by weight, that is, undetectable, but the isomer is typically present in an amount of more than 0% by weight.

EXAMPLES

[0029] The present invention will next be specifically explained with reference to Examples. However, it should not be construed that the present invention is limited to or by Examples.

Example 1

[0030] In a reactor equipped with a stirrer, a distillation column, a side-arm distillation head, a cooling condenser and a thermometer, 2-isopropenyl-5-methyl-4-hexen-1-ol (154.25 g: 1.0 mol), methyl senecioate (136.97 g: 1.2 mol) and titanium(IV) isopropoxide (2.84 g: 0.01 mol) were placed. The resulting mixture was heated at 100°C. Methanol formed as a by-product as the reaction progressed was distilled off through the side-arm distillation head. After the completion of the distillation of methanol, the pressure in the reactor is gradually reduced to 0.133 KPa, the temperature in the reactor was raised to 120°C, and excess methyl senecioate was distilled. Subsequent vacuum distillation provided 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate as the target compound (b.p. of 89-92°C/0.133 KPa, 223.59 g: 0.95 mol, yield of 94.6%, purity of 99.2%).

[0031] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.09% as a result of gas chromatography analysis.

[0032] The structure of the obtained 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate was identified by a ^{1}H-nuclear magnetic resonance spectrum, a ^{13}C-nuclear magnetic resonance spectrum, a mass spectrum and an IR spectrum. The isomer, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, was isolated by a precise preparative capillary gas chromatography system, and the structure was identified by a ^{1}H-nuclear magnetic resonance spectrum, a mass spectrum and an IR spectrum.

<Spectral data of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate>

[0033] Nuclear magnetic resonance spectrum, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.59 (3H, s), 1.67 (3H, s), 1.70 (3H, s), 1.88 (3H, d), 2.00-2.25 (2H, m), 2.15 (3H, d), 2.41 (1H, tt), 4.06 (2H, td), 4.74 (1H, s), 4.82 (1H, s), 5.06 (1H, t) and 5.65 (1H, s).

[0034] ^{13}C-NMR (126 MHz, $CDCl_3$): δ 17.79, 19.94, 20.17, 25.72, 27.34, 28.67, 46.14, 65.09, 112.23, 116.09, 121.73, 132.79, 145.08, 156.37 and 166.70.

[0035] Mass spectrum EI (70 eV): m/z 236 (M^+), 136 ($M^+ - C_4H_7CO_2H$), 121, 107, 95,83,69,55,41 and 29.

[0036] Infrared absorption spectrum (liquid film): ν (cm^{-1}) 850, 891, 1006, 1077, 1145, 1226, 1269, 1347, 1377, 1447, 1650, 1719, 2915 and 2970.

<Spectral data of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate>

[0037] Nuclear magnetic resonance spectrum, ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.60 (3H, s), 1.68 (3H, s), 1.69 (3H, s), 1.80 (3H, d), 2.10-2.29 (2H, m), 2.40 (1H, tt), 3.01 (2H, s), 4.07 (2H, td), 4.73 (1H, s), 4.83 (1H, s), 4.84 (1H, s), 4.90 (1H, s) and 5.06 (1H, t).

[0038] Mass spectrum EI (70 eV): m/z 236 (M^+), 136 ($M^+ - C_4H_7CO_2H$), 121, 107, 93,83,81,69,55,41 and 29.

[0039] Infrared absorption spectrum (liquid film): ν (cm^{-1}) 897, 1009, 1032, 1152, 1245, 1331, 1376, 1449, 1652, 1737, 2851, 2919, 2972 and 3078.

Example 2

[0040] The reaction was carried out in the same manner as in Example 1 except that the amount of titanium(IV)

isopropoxide was 14.20 g (0.05 mol). As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 90-93°C/0.133 KPa, 183.88 g: 0.78 mol, yield of 77.8%, purity of 98.9%) was obtained as the target compound.

[0041] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.11% as a result of gas chromatography analysis.

Example 3

[0042] The reaction was carried out in the same manner as in Example 1 except that ethyl senecioate (153.80 g: 1.2 mol) was used in place of methyl senecioate, and the reaction temperature of the transesterification was 120°C. As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 93-94°C/0.133 KPa, 218.39 g: 0.92 mol, yield of 92.4%, purity of 98.4%) was obtained as the target compound.

[0043] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.10% as a result of gas chromatography analysis.

Example 4

[0044] The reaction was carried out in the same manner as in Example 1 except that the amount of methyl senecioate used was 228.28 g (2.0 mol). As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 90-94°C/0.133 KPa, 219.81 g: 0.93 mol, yield of 93.0%, purity of 99.0%) was obtained as the target compound.

[0045] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.12% as a result of gas chromatography analysis.

Example 5

[0046] The reaction was carried out in the same manner as in Example 1 except that toluene (50.0 ml) was used as the solvent for the transesterification. As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 87-90°C/0.133 KPa, 224.30 g: 0.95 mol, yield of 94.9%, purity of 99.1%) was obtained as the target compound.

[0047] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.10% as a result of gas chromatography analysis.

Example 6

[0048] The reaction was carried out in the same manner as in Example 1 except that dibutyltin oxide (2.48 g: 0.01 mol) was used in place of titanium(IV) isopropoxide. As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 90-93°C/0.133 KPa, 213.19 g: 0.90 mol, yield of 90.2%, purity of 99.0%) was obtained as the target compound.

[0049] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.12% as a result of gas chromatography analysis.

Example 7

[0050] The reaction was carried out in the same manner as in Example 1 except that dibutyltin dichloride (3.04 g: 0.01 mol) was used in place of titanium(IV) isopropoxide. As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 90-93°C/0.133 KPa, 207.52 g: 0.87 mol, yield of 87.8%, purity of 98.8%) was obtained as the target compound.

[0051] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.09% as a result of gas chromatography analysis.

Example 8

[0052] The reaction was carried out in the same manner as in Example 1 except that aluminum isopropoxide (2.04 g: 0.01 mol) was used in place of titanium(IV) isopropoxide. As a result, 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (b.p. of 90-93°C/0.133 KPa, 210.59 g: 0.89 mol, yield of 89.1%, purity of 98.6%) was obtained as the target compound.

[0053] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 0.10% as a result of gas chromatography analysis.

Comparative Example 1

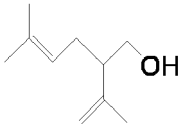
[0054] In a reactor equipped with a stirrer, a cooling condenser and a thermometer, 2-isopropenyl-5-methyl-4-hexen-1-ol (154.25 g: 1.0 mol), triethylamine (122.44 g: 1.21 mol) and toluene (775.6 g) were placed. The resulting mixture was cooled at 5°C. Methanesulfonyl chloride (137.46g: 1.20 mol) was added dropwise thereto over 2 hours, while keeping the reaction solution at 20°C or lower. After the dropwise addition was over, the temperature of the reaction solution was increased to 25°C, and then the reaction solution was stirred for 1 hour. The reaction was stopped by addition of water (462.4 g) into the reaction solution, and the water phase was removed. The organic phase was washed with 5% by weight aqueous sodium hydrogen carbonate solution, followed by water (464.1 g). The organic phase was subjected to removal of solvent under reduced pressure, and then provided 2-isopropenyl-5-methyl-4-hexen-1-yl methanesulfonate (225.72 g: 0.98 mol, yield of 98.0%, purity of 97.8%).

[0055] In a reactor equipped with a stirrer, a cooling condenser and a thermometer, senecionic acid (111.13 g: 1.11 mol), potassium carbonate (105.04 g: 0.76 mol), tetrabutylammonium chloride (11.39 g: 0.04 mol), water (9.1 g) and toluene (765.7 g) were placed. The resulting mixture was stirred at 90 to 95°C for 30 minutes. After the stirring, a solution of the above 2-isopropenyl-5-methyl-4-hexen-1-yl methanesulfonate (230.33 g: 1.0 mol) in toluene (797.1 g) was added dropwise thereto over 10 hours. After the dropwise addition was over, the resulting mixture was stirred at 90 to 95°C for 6 hours. The reaction was stopped by addition of water (698.2 g) into the reaction solution, and the water phase was removed. The organic phase was washed with water (465.8 g). The organic phase was subjected to removal of solvent under reduced pressure, and then distilled under reduced pressure to obtain 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate (203.26 g: 0.86 mol, yield of 86.2%, purity of 95.5%) was obtained.

[0056] The content of 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-3-butenoate, which was an isomer contained by the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate fraction, was 1.87% as a result of gas chromatography analysis.

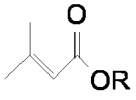
Claims

1. A method for producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate, comprising a step of transesterifying 2-isopropenyl-5-methyl-4-hexen-1-ol represented by Formula (1):



(1)

with alkyl senecioate represented by General Formula (2):

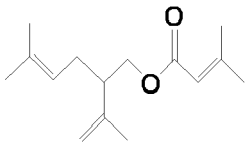


(2)

wherein R is a saturated or unsaturated linear alkyl group having 1 to 6 carbon atoms, in the presence of a catalyst, while distilling off an alcohol represented by General Formula (4):

ROH (4)

formed as a by-product, to obtain the 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate represented by Formula (3):



(3)

2. The method for producing 2-isopropenyl-5-methyl-4-hexen-1-yl 3-methyl-2-butenoate according to claim 1, wherein the catalyst is a Lewis acid containing a titanium atom, a tin atom or an aluminum atom.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 19 7129

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	14 April 2016	Bedel, Christian

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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